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<p>(21) International Application Number: <b>PCT/SE96/00873</b></p> <p>(22) International Filing Date: <b>1 July 1996 (01.07.96)</b></p> <p>(30) Priority Data: <b>9502631-6 17 July 1995 (17.07.95) SE</b></p> <p>(71) Applicant (<i>for all designated States except US</i>): <b>SVERIGES STÄRKELSEPRODUCENTER, FÖRENING UPA [SE/SE]; P.O. Box 75, S-374 22 Karlshamn (SE).</b></p> <p>(72) Inventor; and (75) Inventor/Applicant (<i>for US only</i>): <b>WIKSTRÖM, Olle [SE/SE]; Vasagatan 1, S-291 53 Kristianstad (SE).</b></p> <p>(74) Agent: <b>AWAPATENT AB; P.O. Box 5117, S-200 71 Malmö (SE).</b></p>		<p>(81) Designated States: <b>AL, AM, AT, AT (Utility model), AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>With international search report. In English translation (filed in Swedish).</i></p>	
<p>(54) Title: <b>FINISHING AGENT</b></p> <p>(57) Abstract</p> <p>The use of amylopectin-type starch obtained from potato that has been subjected to a genetical engineering modification to suppress the formation of amylose-type starch, as a finishing agent in papermaking is described.</p>			

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FINISHING AGENT

The present invention relates to the use of amylopectin-type starch or derivatives thereof as a finishing agent in papermaking.

More specifically, the present invention relates to  
5 the use of amylopectin-type starch obtained from potato  
that has been modified by genetical engineering, to suppress  
the formation of amylose-type starch.

Background of the Invention

In the manufacture of paper and paperboard intended  
10 for some kind of printing the print-receiving surface is  
treated either by a pure starch solution or by a coating  
slip. When traditional starch of any known origin (potato,  
maize, wheat and tapioca) is used, more than one chemical  
modification step is required in many cases to obtain a  
15 product possessing sufficient stability. The various  
modification steps usually include a stabilising step, for  
instance an etherification reaction with propene dioxide  
or an esterification reaction with vinyl acetate or acetic  
anhydride, and a degradation step, such as oxidation, en-  
20 zymatic degradation, acid hydrolysis or so-called thermo-  
chemical conversion. During the above steps substitution  
of the starch takes place, and the degree of substitution  
pertaining to the corresponding stabilising step usually  
amounts to 0.01 - 0.5 mole/mole glucose, preferably  
25 0.05 - 0.20 mole/mole.

The necessity to carry out more than one modification step entails costs and has negative effects on the environment, and a reduction of the required number of chemical modification steps thus is desirable.

30 Object of the Invention

The object of the present invention is to reduce the number of chemical modification steps necessary to obtain a stable finishing agent for use on paper. This object is achieved by using amylopectin-type starch of the kind out-

lined in the introduction, which starch additionally possesses the characteristics defined in the appended claims.

Summary of the Invention

In accordance with the present invention amylo-  
5 pectin-type starch or derivatives thereof thus are used  
as a finishing agent in papermaking.

The expression "amylopectin-type starch" as used throughout in the present application text relates to starch obtained from potato that has been submitted to  
10 genetical engineering in order to suppress the formation of amylose-type of starch. The expression "derivatives thereof" relates to chemically, physically and/or enzymatically derivatised amylopectin-type starch. The amylopectin content of amylopectin-type starch is in excess  
15 of 95%, preferably in excess of 98%. The remaining ingredient in amylopectin-type starch is amylose.

A detailed description of the above amylopectin-type starch and derivatives thereof and the methods of their production is found in the Swedish Patent Specification  
20 9004096-5 (Amylogene HB).

When practising the invention, amylopectin-type starch is added in amounts of 0.5-8% by weight, preferably 2-6% by weight, during the production process.

By means of the present invention it thus becomes  
25 possible to eliminate the above-mentioned stabilising step, since the amylopectin in the starch used in accordance with the invention, having strongly reduced amylose contents on account of its branched structure, possesses excellent stability. Thus, only one chemical reaction is  
30 required to produce the finishing agent, and consequently surface-sizing and coating products may be manufactured in a manner that is considerably less harmful to the environment than has hitherto been possible. The reason therefor is not only the elimination of the modification  
35 step but also that it has become possible to alter the degradation step. In consequence of this alteration the amount of oxidising agent required to degrade the amylo-

pectin in the starch used in accordance with the invention is approximately 50% lower than the amount required to degrade traditional potato starch. In general, sodium hypochlorite, hydroperoxide or some type of persulphate 5 compound, such as sodium persulphate, is used as the degradation chemical.

It is not previously known to use amylopectin-type starch as a finishing agent for use on paper. Practical tests have shown, however, that the use of amylopectin-10 type starch gives surprising and unexpected combined effects inasmuch as it permits the finishing agent to be produced by a simplified as well as environmentally less harmful method.

The invention will be explained in greater detail in 15 the following by means of the Examples below.

Example 1

Oxidised starch based on potato starch was produced in the following manner. 100 kg potato starch were formed into a slurry in water. The pH-value of the slurry was 20 adjusted to 9.5 by means of sodium hydroxide. 23.4 litres of sodium hypochlorite containing an active substance of 150 g/litre active chlorine were added. The pH-value of the reaction was maintained constant by addition of sodium hydroxide. Once the reaction was complete, i.e. 25 when all chlorine had been used up, the reaction was interrupted by neutralisation, by means of hydrochloric acid, to a pH-value of 5.5, whereupon the product was de-watered and washed before drying. The following values were obtained from an analysis of the product:

30	Dry contents, %	82.4
	pH of slurry	8.0
	pH of solution	6.4
	Conductivity, $\mu$ S/cm	155
	Contents of carboxyl, %	0.87
35	Viscosity at different temperatures	
	Viscosity, cP, 25%, 100 rpm	80 °C 80
		70 °C 95

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50 °C	135
30 °C	232

**Viscosity at different concentrations**

5	Viscosity, cP, 50 °C, 100 rpm	10%	26
		15%	47
		20%	76
		25%	135
		30%	343
10		35%	600

**Stability**

15	Viscosity, cP, 25%, 25 °C, 100 rpm	0 min	350
		60 min	580
		120 min	780
		180 min	1250
		1 day	firm gel formed

20        At comparatively high concentration levels (25%), the product exhibits very poor stability at low temperatures (25 °C), and already after the lapse of two h the viscosity is more than doubled. This behaviour is typical in traditional oxidised starches, and these products can  
 25        only be used at low concentration levels and when the temperature is at least 50 °C.

Example 2

30        Oxidised amylopectin starch from potato was produced in the following manner. 100 kg amylopectin-type starch was formed into an aqueous slurry. The pH value of the slurry was adjusted to 9.5 by means of sodium hydroxide. 11.0 litres of sodium hypochlorite containing an active substance of 150 g/litre active chlorine was added. The pH value of the reaction was maintained constant by addition  
 35        of sodium hydroxide. Once the reaction was completed, i.e. when all chlorine had been consumed, the reaction was interrupted by neutralisation, by means of hydrochloric

## 5

acid, to a pH value of 5.5, whereupon the product was dewatered and washed before drying. The following values were obtained in an analysis of the product:

Dry contents, %	83.5	
5 pH of slurry	8.0	
pH of solution	6.1	
Conductivity, $\mu\text{S}/\text{cm}$	149	
Contents of carboxyl, %	0.76	
Viscosity at different temperatures		
10 Viscosity, cP, 25%, 100 rpm	80°C	78
	70°C	92
	50°C	131
	30°C	198
15 Viscosity at different concentrations		
Viscosity, cP, 50°C, 100 rpm	10%	24
	15%	44
	20%	73
	25%	116
20	30%	203
	35%	603
Stability		
Viscosity, cP, 25%, 25°C, 100 rpm	0 min	267
25	60 min	267
	120 min	267
	180 min	270
	1 day	311
	2 days	315
30	3 days	350

The stability of the product is highly satisfactory, also at low temperatures (25°C), and the viscosity had increased only marginally after storage of the product 35 for up to 3 days. The product may be used without difficulty in high concentrations, also if the temperature is allowed to become lower. This is possible in the case of

products having potato starch as its base only if the product is stabilised by an esterification or etherification reaction.

## CLAIMS

1. The use of amylopectin-type starch obtained from 5 potato that has been modified by genetical engineering to suppress the formation of amylose-type starch, as a finishing agent in papermaking.
2. The use in accordance with claim 1, wherein the amylopectin-type starch contains more than 95% amylopectin, preferably more than 98% amylopectin. 10
3. The use in accordance with claim 1, wherein a derivative of chemically, physically and/or enzymatically derivatised amylopectin-type starch is added as a finishing agent.
4. The use according to any one of the preceding 15 claims, wherein the amylopectin-type starch or derivatives thereof is added in amounts of 0.5-8% by weight, preferably 2-6% by weight.
5. The use according to any one of the preceding 20 claims, wherein the amylopectin-type starch is subjected to oxidation, enzymatic treatment, acid hydrolysis or thermo-chemical conversion.
6. The use as claimed in claim 5, wherein the 25 thermo-chemical conversion is effected by means of compounds of persulphate or peroxide.

1  
INTERNATIONAL SEARCH REPORTInternational application No.  
PCT/SE 96/00873

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21H 17/28, D21H 19/12, D21H 19/54  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS, JAPIO, PAPERCHEM

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1028758 A (NATIONAL STARCH AND CHEMICAL CORPORATION), 4 May 1966 (04.05.66), page 3, line 19 - line 32, claim 1 --	1-6
A	EP 0353212 A1 (W.R. GRACE & CO.-CONN.), 31 January 1990 (31.01.90), page 3, line 36 - line 60, abstract --	1-6
A	WO 9211376 A1 (AMYLOGENE HB), 9 July 1992 (09.07.92), page 1, claims 1-3, abstract --	1-6

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search  
  
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5365016 A (MICHAEL M. BURRELL ET AL), 15 November 1994 (15.11.94), column 1, line 9 - line 15; column 2, line 54 - line 59, claim 1  -- -----	1-6

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

01/10/96

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